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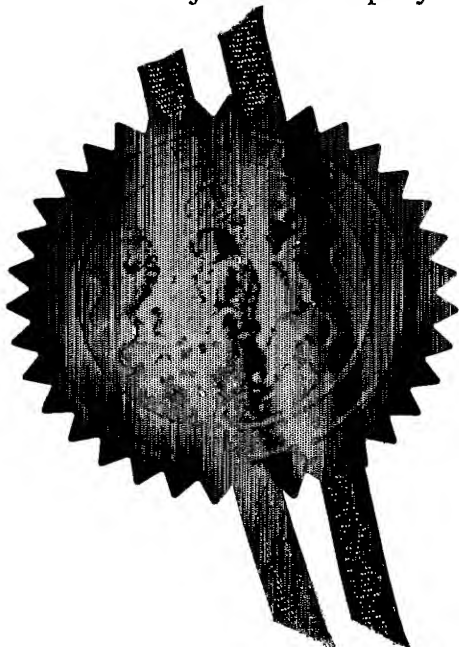
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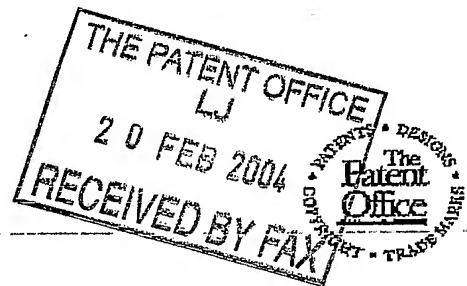
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**The BOC Group plc, Chertsey Road, Windlesham, Surrey, GU20 6HJ**

Patents ADP number (if you know it)

**884627002** ✓

If the applicant is a corporate body, give the country/state of its incorporation

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4. Title of the invention  
**GAS ABATEMENT**

5. Name of your agent (if you have one)  
**Andrew Steven BOOTH**

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Signature(s)

Michael Wickham

Date 20/02/2004

## 12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

Mike Wickham  
(01276) 807612

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### GAS ABATEMENT

The present invention relates to gas abatement. The invention finds particular use in the abatement of gases exhaust from a process tool used in the semiconductor manufacturing industry.

CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, NF<sub>3</sub> and SF<sub>6</sub> are commonly used in the semiconductor manufacturing industry, for example, in dielectric film etching. Following the manufacturing process there is typically a residual PFC content in the effluent gas pumped from the process tool. PFCs are difficult to remove from the effluent gas, and their release into the environment is undesirable because they are known to have relatively high greenhouse activity.

The object of abatement is to convert the PFCs into one or more compounds that can be more conveniently disposed of, for example, by conventional scrubbing.

Plasma abatement has proved to be an effective method for degradation of PFCs to less damaging species. In the plasma abatement process, an effluent gas containing the PFCs to be destroyed is caused to flow into a high density plasma. Under the intensive conditions within the plasma, the PFCs are subjected to impact with energetic electrons causing dissociation into reactive species. These species can combine with oxygen or hydrogen added to the effluent gas to produce relatively stable, low molecular weight by-products, for example, CO, CO<sub>2</sub> and HF, which can then be removed in a further treatment step utilising, for example, a wet scrubber to take the HF into aqueous solution.

However, known plasma abatement techniques tend to be relatively complex and have relatively high energy requirements. For example, in one known plasma abatement technique, the effluent gas stream is conveyed into a resonant cavity using microwave radiation to generate, from the PFCs, a microwave plasma. Another known technique is to convey the effluent stream into a dielectric tube, a

high frequency surface-wave exciter being used to produce surface waves which generate a plasma within the tube to dissociate the PFCs.

5 In another PFC abatement technique, the effluent waste stream is brought into contact with a superheated stream of water vapour for reacting with the PFCs within the waste stream. However, such a technique not only requires heating of the water vapour to a temperature of at least 150°C, but also requires the effluent stream to be subsequently conveyed through a heat exchange mechanism to cool  
10 the stream before it is conveyed to a wet scrubber, the efficiency of the scrubber decreasing as a function of increasing temperature.

It is an aim of at least the preferred embodiment of the present invention to provide a relatively simple and efficient technique for treating an effluent fluid stream.

15 In a first aspect, the present invention provides a method of treating an effluent fluid stream from a semiconductor manufacturing process tool, the method comprising injecting an ionised fluid stream into a reaction chamber, and conveying the effluent fluid stream to the chamber, wherein the ionised fluid stream either contains reactive species for reacting with a component of the  
20 effluent fluid stream, or impinges upon a reactive fluid conveyed to the chamber to form the reactive species.

By providing a method in which reactive species are formed from the reactive fluid for subsequent reaction with the component in the effluent waste stream, it has  
25 been found that the energy required to cause the destruction of the component in the waste stream, and the efficiency of that destruction, can be radically improved. For example,  $H^+$  and  $OH^-$  ions formed from the dissociation of water are capable of reacting with, for example, a PFC contained in the waste stream at ambient temperature, and thus at a much lower temperature than would be required if the  
30 water had not been pre-ionised before being introduced into the waste stream.

Another advantage is provided by not bringing the equipment used to generate the ionised fluid stream into contact with either the effluent waste stream or any by-products from the reaction of the reactive species with the component of the waste stream. As a result, any one of a range of equipment may be used to generate the ionised fluid stream. In the preferred embodiment, a plasma is generated to decompose a fluid to produce the ionised fluid stream. For example, the plasma may be generated using a D.C source or radiation at a frequency of around 580 kHz, 13.56 MHz, 27 MHz, 915 MHz or 2.45 GHz to generate from the fluid a plasma to form the ionised fluid stream. Alternatively, a glow discharge may be generated to decompose the fluid. As is well known, a glow discharge is a luminous, thermal plasma formed by applying to a gas a voltage that is greater than the breakdown voltage of that gas. The ionised fluid stream may also be generated by a discharge other than a glow discharge, for example by a corona discharge or an arc discharge. Such a discharge may be generated using a plasma gun, in which an electric arc is created between a water cooled nozzle (anode) and a centrally located cathode. A stream of fluid passes through the electric arc and is dissociated thereby. The plasma of ionised fluid issuing from the nozzle resembles an open oxy-acetylene flame.

Further advantages are that a relatively cheap and readily available fluid, such as water vapour or a fuel, for example methane or an alcohol, can be used to generate  $H^+$  and/or  $OH^-$  ions, as the reactive species, and that the reaction can take place at any convenient pressure, for example, at or around atmospheric pressure.

Two different techniques may be used to form the reactive species using a plasma gun. In the first technique, the ionised fluid stream is formed from the reactive fluid. An electric arc is established between electrodes of the gun and the reactive fluid is conveyed along the arc to generate a flame containing the reactive species. This flame is subsequently injected into the chamber to abate the effluent fluid stream within. In the second technique, the ionised fluid stream is formed from a source gas different from the reactive fluid. For example, an inert



ionisable gas, such as nitrogen or argon, can be conveyed along the arc to generate the flame for injection into the effluent waste stream. Both the reactive fluid and the effluent waste stream are separately conveyed into the chamber. The reactive fluid is dissociated by the flame to form the reactive species within the chamber, which species subsequently react with the component of the waste stream.

In the preferred embodiment, a single plasma gun is used to inject the ionised fluid stream into the effluent waste stream. However, a plurality of such guns may be provided to inject a plurality of ionised fluid streams either into the same waste stream or into respective streams. This can increase further the efficiency of the treatment of the waste stream. These guns may be connected to a common power source or to respective sources.

Depending on whether the chamber is connected to the inlet or the outlet of a pump for pumping the effluent stream from the process tool, and the flow rate of the effluent fluid stream, the chamber may be at any pressure in the range from  $10^{-3}$  mbar to 2000 mbar.

Depending on the nature of the reaction occurring within the chamber, the abatement of the compound(s) within the effluent fluid stream may be promoted by heating the chamber, for example, to a temperature in the range from ambient to  $1500^{\circ}\text{C}$ . For example, the abatement of hydrides and organometallic compounds can be promoted by heating the chamber to a temperature in the range from  $400^{\circ}\text{C}$  to  $1500^{\circ}\text{C}$ , more preferably in the range from  $500^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$ .

The ionised fluid stream may be injected into the effluent fluid stream over a catalyst, for example, one of tungsten, silicon and iron.

The effluent fluid stream is preferably subsequently conveyed to a wet scrubber or a reactive solid media downstream from the chamber to remove one or more by-

products from the reaction from the effluent stream. The scrubber may be coupled close to the reaction chamber, or may be more remote from the reaction chamber.

As previously mentioned, the component of the effluent fluid stream may comprise  
5 a perfluorinated, or a hydrofluorocarbon, compound, for example, one of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CHF}_3$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_8$ ,  $\text{NF}_3$  and  $\text{SF}_6$ .

In a second aspect, the present invention provides a method of treating an effluent  
fluid stream from a semiconductor manufacturing process tool, the method  
10 comprising thermally decomposing a stream of fluid into one or more reactive species, and injecting the reactive species into the effluent fluid stream for reacting with a component of the effluent fluid stream.

In a third aspect, the present invention provides a method of treating an effluent  
15 fluid stream from a semiconductor manufacturing process tool, the method comprising injecting an ionised fluid stream into a reaction chamber, and conveying into the reaction chamber a first stream containing the effluent fluid and a second stream containing a reactive fluid, wherein the ionised fluid stream  
impinges upon the reactive fluid to form reactive species for reacting with a  
20 component of the effluent fluid stream.

Preferred features of the present invention will now be described with reference to the accompanying drawings, in which:

25 Figure 1 is an illustration of an apparatus for treating an effluent waste stream;

Figure 2 is an illustration of one embodiment of a plasma torch for generating an ionised fluid stream for injection into the waste stream; and

30 Figure 3 is an illustration of another embodiment of a plasma torch for generating an ionised fluid stream for injection into the waste stream.

With reference to Figure 1, an example of an apparatus for treating an effluent waste stream comprises a reaction chamber 10 having a first inlet 12 for receiving the waste stream from a process tool (not shown), a second inlet 14 for receiving a stream of reactive fluid for reacting with a component of the waste stream, and an outlet 16 for exhausting from the chamber 10 a fluid stream containing by-products from the reaction between the reactive fluid and the component of the waste stream.

The reaction chamber 10 is further provided with a dc plasma torch 18 for generating an ionised fluid stream for injection into the chamber 10 to convert the reactive fluid into reactive species. Figure 2 shows in more detail the configuration of one arrangement for the plasma torch 18. The plasma torch 18 comprises an elongate tubular electron emitter 20 having an end wall 22. Water coolant 24 is conveyed through the bore 26 of the electron emitter 20 during use of the torch 18.

The bore 26 of the electron emitter 20 is aligned with a nozzle 28 formed in a start electrode 30 surrounding the end wall 22 of the electron emitter 20. The start electrode 30 is mounted in an insulating block 32 surrounding the electron emitter 20. A bore 34 formed in the block 32 conveys a stream of plasma source gas 36, for example, nitrogen or argon, into a cavity 38 located between the end wall 22 of the electron emitter 20 and the start electrode 30.

In operation of the plasma torch 18, a pilot arc is first generated between the electron emitter 20 and the start electrode 30. The arc is generated by a high frequency, high voltage signal typically provided by a generator associated with the power supply for the torch. This signal induces a spark discharge in the source gas flowing in the cavity 38, and this discharge provides a current path. The pilot arc thus formed between the electrode emitter 20 and the start electrode 30 ionises the source gas passing through the nozzle 28 to produce a high momentum plasma flame of ionised source gas from the tip of the nozzle 28. The

flame passes from the nozzle towards an anode 40 surrounding the nozzle 28 to define a plasma region 42.

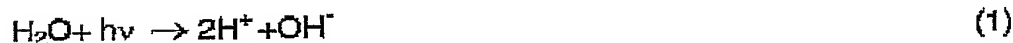
Anode 40 has a first fluid inlet 44 for receiving the reactive fluid stream entering the chamber 10 via chamber inlet 12, and a second fluid inlet 46 for receiving the waste stream entering the chamber 10 via chamber inlet 14. In use, the reactive fluid is dissociated by the flame to form reactive species within the plasma region 42. These reactive species subsequently react with a component of the waste stream conveyed into the plasma region 42. The by-products from the reaction are exhaust from the plasma region 42 through outlet 48, and subsequently exhaust from the chamber via chamber outlet 16 to a wet scrubber.

Figure 3 illustrates an alternative arrangement for generating the ionised fluid stream. In this arrangement, the stream of reactive fluid is conveyed directly to the plasma torch 18, rather than into the body of the plasma chamber 10. As shown in Figure 3, the reactive fluid stream is conveyed into the bore 26 of the electron emitter 20. The reactive fluid stream passes from the end of the electron emitter 20 into the cavity 38, where it is ionised by the plasma flame created from the source gas 36 to form a stream of reactive species which are injected from the nozzle 28 into the plasma region 42 to react with the component of the waste stream conveyed into the plasma region 42. In this arrangement, water coolant is conveyed within a jacket 50 surrounding the electron emitter 20.

Some examples of reactions occurring within the plasma region will now be described.

#### Example 1

The reactive fluid is a source of  $H^+$  and  $OH^-$  ions, for example, water vapour, and the waste stream contains a perfluorocompound, for example,  $CF_4$ . The plasma flame dissociates the water vapour into  $H^+$  and  $OH^-$  ions:



which react with perfluorocompound to form carbon dioxide and HF as by-products:



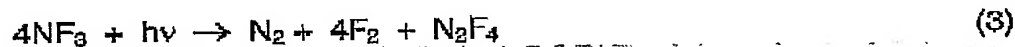
The waste stream containing the by-products is subsequently conveyed to a wet scrubber to take the HF into aqueous solution, or to a solid reaction media for reaction with the HF to form a solid by-product which can be readily disposed of.

A typical gas mixture for performing a dielectric etch in a process tool may contain differing proportions of the gases  $\text{CHF}_3$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_8$  or other perfluorinated or hydrofluorocarbon gas, but the chemical reactions of the  $\text{H}^+$  and  $\text{OH}^-$  ions with these components of the waste gas stream will differ in detail but the general form will be as the scheme above.

### Example 2

The reactive fluid is again a source of  $\text{H}^+$  and  $\text{OH}^-$  ions, for example, water vapour, and the waste stream contains  $\text{NF}_3$ . Process tool manufacturers are increasingly adopting  $\text{NF}_3$  as the chamber cleaning gas of choice for PECVD reactors.

Whereas the utilisation of  $\text{NF}_3$  by the cleaning process is much higher than that of either  $\text{CF}_4$  or  $\text{C}_2\text{F}_6$ , the by-products produced are considerably more reactive and their uncontrolled release is potentially very dangerous. Some examples of plasma by-products and their reactions are detailed below.



Example 3

It is normal practice to introduce materials such as silicon, phosphorous, arsenic into a process tool as both inorganic hydrides or organometallic compounds. Other materials such as silicon, tantalum, aluminium, copper are introduced into the process chamber as organometallic compounds. In other process steps by-products of reaction are known to make powders that are very reactive and present a substantial danger if they collect in quantity, as they have been known to spontaneously react causing equipment damage.

The introduction of a reactive ion agents directly into the waste gas has been shown to substantially reduce the reactivity of such compounds, rendering them safe for subsequent handling.

The reactions are further enhanced by maintaining the reaction chamber at an elevated temperature in the range of 400°C to 1500°C, but preferably in a temperature range 500°C to 1000°C.

In summary, a method is described for treating an effluent fluid stream from a semiconductor manufacturing process tool. In one embodiment, a plasma torch is used to thermally dissociate a stream of water vapour into  $H^+$  and  $OH^-$  ions. A stream containing the ions is then injected into the effluent fluid stream to react with a perfluorocompound within the fluid stream. In another embodiment, the plasma torch is used to generate an ionised stream from an inert gas. This ionised stream is injected into a reaction chamber, which receives both the stream of water vapour and the effluent fluid stream. The ionised stream dissociates the water vapour into  $H^+$  and  $OH^-$  ions for reaction with the perfluorocompound.

CLAIMS

1. A method of treating an effluent fluid stream from a semiconductor manufacturing process tool, the method comprising injecting an ionised fluid stream into a reaction chamber, and conveying the effluent fluid stream to the chamber, wherein the ionised fluid stream either contains reactive species for reacting with a component of the effluent fluid stream, or impinges upon a reactive fluid conveyed to the chamber to form the reactive species.
2. A method according to Claim 1, wherein the ionised fluid stream contains the reactive species.
3. A method according to Claim 2, wherein the reactive species are formed by thermally decomposing the reactive fluid.
4. A method according to Claim 3, wherein a plasma is created to decompose the reactive fluid.
5. A method according to Claim 1, wherein the ionised fluid stream impinges upon a reactive fluid conveyed into the chamber to form the reactive species.
6. A method according to Claim 5, wherein the ionised fluid stream is formed from a stream of source gas.
7. A method according to Claim 6, wherein the source gas comprises an inert ionisable gas, for example, nitrogen and/or argon.
8. A method according to Claim 6 or Claim 7, wherein a plasma is created to decompose the source gas.

9. A method according to Claim 4 or Claim 8, wherein the plasma is generated at or around atmospheric pressure.
10. A method according to Claim 9, wherein the plasma is a glow, corona or arc discharge.
11. A method according to Claim 10, wherein the plasma is generated using a dc plasma torch.
12. A method according to any preceding claim, wherein the reactive species comprise  $\text{OH}^\cdot$  and/or  $\text{H}^\cdot$  ions.
13. A method according to any preceding claim, wherein the reactive fluid comprises water or water vapour.
14. A method according to any of Claims 1 to 12, wherein the reactive fluid comprises an alcohol.
15. A method according to Claim 14, wherein the alcohol comprises one of methanol, ethanol, propanol, propan-2-ol and butanol.
16. A method according to any of Claims 1 to 12, wherein the reactive fluid comprises one of  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$  and a paraffin.
17. A method according to any of Claims 1 to 11, wherein the reactive species comprise oxygen radicals.
18. A method according to Claim 17, wherein the reactive fluid comprises one of oxygen and/or ether.
19. A method according to any preceding claim, wherein the chamber is at a temperature in the range from ambient to  $1200^\circ\text{C}$ .



20. A method according to Claim 19, wherein the chamber is at ambient temperature.

5 21. A method according to Claim 19, wherein the chamber is at a temperature in the range from 400°C to 1000°C.

22. A method according to any preceding claim, wherein the chamber is at a pressure in the range  $10^{-3}$  mbar to 2000 mbar.

10

23. A method according to Claim 22, wherein the chamber is at a pressure at or around atmospheric pressure.

24. A method according to any preceding claim, wherein the ionised fluid stream is injected into the chamber over a catalyst.

15

25. A method according to Claim 24, wherein the catalyst comprises one of tungsten, silicon iron rhodium and platinum.

20

26. A method according to any preceding claim, wherein the effluent fluid stream is subsequently conveyed from the chamber to a wet scrubber.

25

27. A method according to any preceding claim, wherein the effluent fluid stream is subsequently conveyed from the chamber to a reactive media.

28. A method according to any preceding claim, wherein the component of the effluent fluid stream comprises a perfluorinated or hydrofluorocarbon compound.

30

29. A method according to Claim 28, wherein the component comprises one of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CHF}_3$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_8$ ,  $\text{NF}_3$  and  $\text{SF}_6$ .
30. A method according to any of Claims 1 to 27, wherein the component of the effluent fluid stream comprises an organometallic.
31. A method according to any of Claims 1 to 27, wherein the component of the effluent fluid stream comprises an inorganic hydride.
32. A method of treating an effluent fluid stream from a semiconductor manufacturing process tool, the method comprising thermally decomposing a stream of fluid into one or more reactive species, and injecting the reactive species into the effluent fluid stream for reacting with a component of the effluent fluid stream.
33. A method of treating an effluent fluid stream from a semiconductor manufacturing process tool, the method comprising injecting an ionised fluid stream into a reaction chamber, and conveying into the reaction chamber a first stream containing the effluent fluid and a second stream containing a reactive fluid, wherein the ionised fluid stream impinges upon the reactive fluid to form reactive species for reacting with a component of the effluent fluid stream.

**ABSTRACT**

A method is described for treating an effluent fluid stream from a semiconductor manufacturing process tool. In one embodiment, a plasma torch is used to thermally dissociate a stream of water vapour into  $H^+$  and  $OH^-$  ions. A stream containing the ions is then injected into the effluent fluid stream to react with a perfluorocompound within the fluid stream. In another embodiment, the plasma torch is used to generate an ionised stream from an inert gas. This ionised stream is injected into a reaction chamber, which receives both the stream of water vapour and the effluent fluid stream. The ionised stream dissociates the water vapour into  $H^+$  and  $OH^-$  ions for reaction with the perfluorocompound.

(Figure 1)

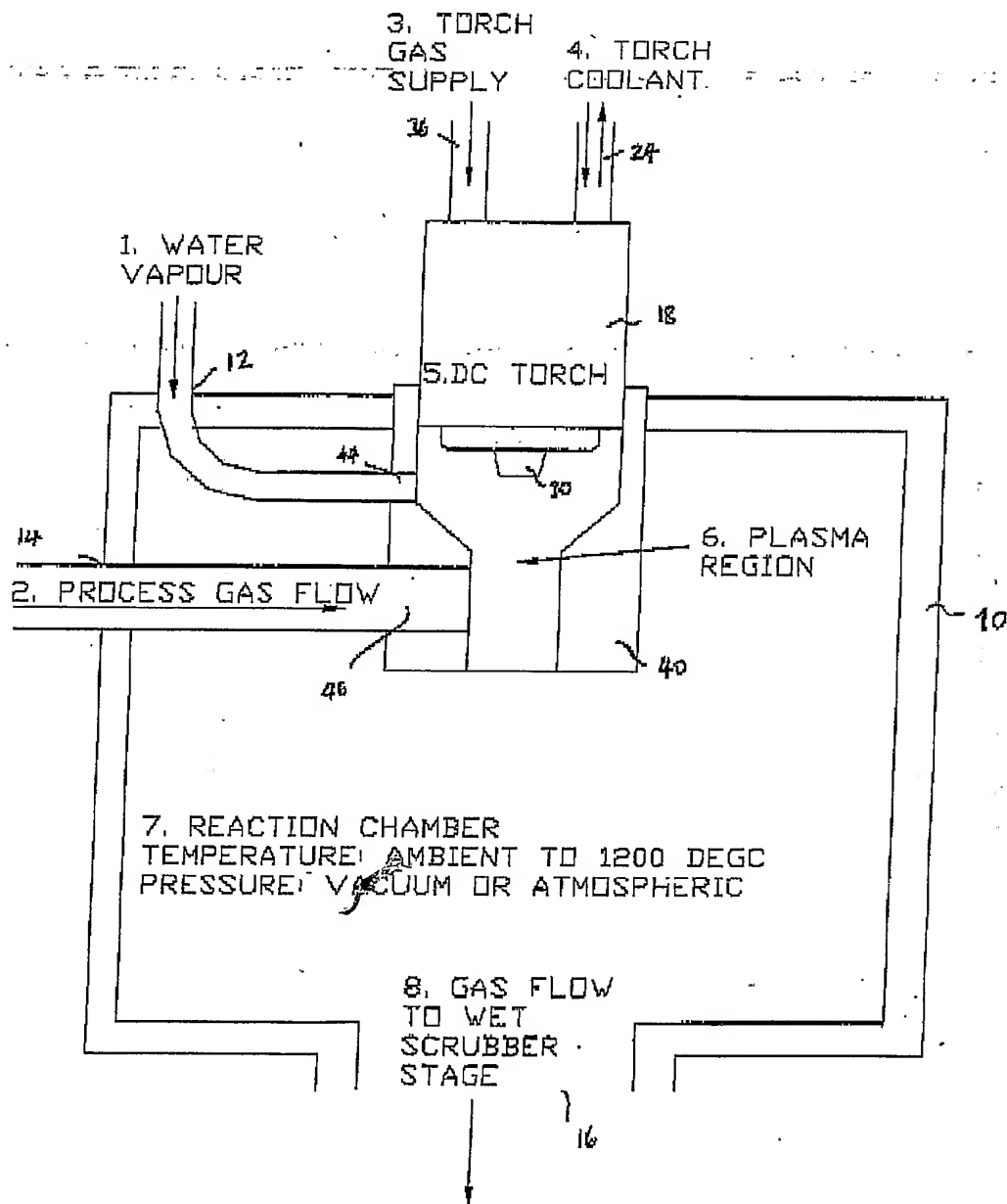


FIGURE 1

Figure 1: Reaction Chamber Concept



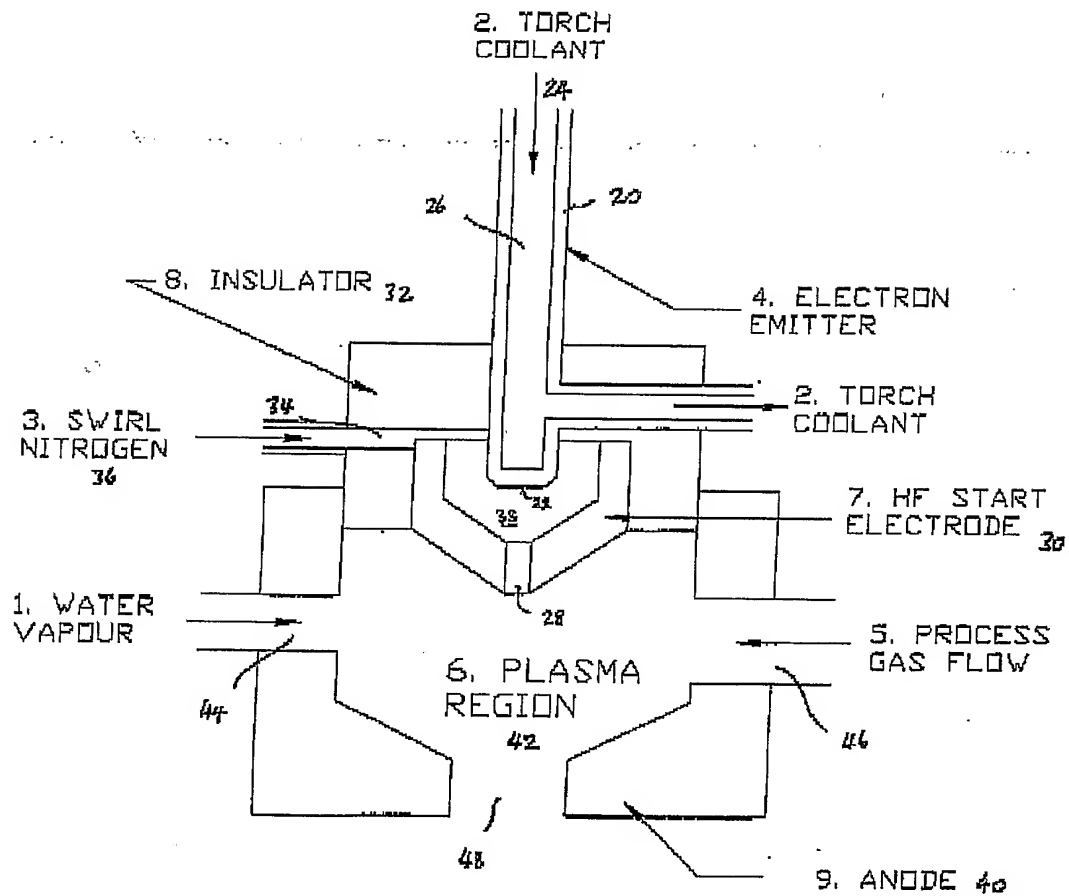


FIGURE 2

~~Figure 3: DC Plasma Torch (Water Vapour Introduced Through Torch)~~







